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(21) International Application Number: PCT/US94/03037 (22) International Filing Date: 22 March 1994 (22.03.94) (30) Priority Data: 039,756 30 March 1993 (30.03.93) US (71) Applicant: UNIROYAL CHEMICAL COMPANY, INC. [US/US]; World Headquarters, Middlebury, CT 06749 (US). (72) Inventors: BARRY, Lawrence, B.; 75 Ponderosa Lane, Newington, CT 06111 (US). ROWLAND, Robert, G.; 177 Newton Road, Woodbridge, CT 06525 (US). RICHARDSON, Mark, C.; 359 Dryden Drive, Cheshire, CT 06410 (US). (74) Agents: THOMPSON, Raymond, D. et al.; Uniroyal Chemical Company, Inc., World Headquarters, Middlebury, CT 06749 (US).		(81) Designated States: AU, BR, CA, CZ, FI, JP, KR, KZ, RU, UA, UZ, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: METHOD FOR STABILIZING AN ORGANIC MATERIAL WHICH IS SUBJECT TO THERMAL AND/OR OXIDATIVE DETERIORATION AND RESULTING STABILIZED MATERIAL (57) Abstract Organic materials which are subject to thermal and/or oxidative deterioration, e.g., polyether polyols and polyurethane foams prepared from polyether polyols, are stabilized against such deterioration by the addition thereto of a stabilizing amount of a liquid, crystallization-resistant mixture of phenolic esters made up predominantly of phenolic monoester(s), the mixture of phenolic esters being obtained by reacting an alkyl ester of a 3,5-dialkyl-4-hydroxyphenyl alkanolic acid with a polyhydroxyl alcohol under esterification reaction conditions employing an esterification reaction catalyst.		

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1 METHOD FOR STABILIZING AN ORGANIC MATERIAL WHICH
 IS SUBJECT TO THERMAL AND/OR OXIDATIVE
 DETERIORATION AND RESULTING STABILIZED MATERIAL

BACKGROUND OF THE INVENTION

5 This invention relates to methods for
 stabilizing organic materials which are prone to
 deterioration via thermal and/or oxidative mechanisms and
 to the resulting stabilized materials. More particularly,
 the invention relates to such methods and compositions
10 which employ hindered phenols as stabilizers.

 Prior art methods for the stabilization of
 polyether polyols and other polymeric materials with
 antioxidants or other stabilizers and the use of the
 stabilized polyols in the preparation of polyurethane
15 foams to inhibit scorch are well known. Polyether
 polyols, used in the manufacture of slabstock flexible and
 semiflexible polyurethane foams, are typically stabilized
 with antioxidant packages consisting of phenolic and amine
 antioxidants which may also contain synergists such as
20 phenothiazine or various compounds containing phosphite
 moieties.

 U.S. Patent Nos. 3,567,664 and 3,637,865
 disclose the use of a mixture of 2,6-di-tert-butyl-4-
 methyl phenol, also referred to as butylated
25 hydroxytoluene, or BHT, and p,p'-dialkyldiphenylamines to
 stabilize polyurethane foams. While BHT has been widely
 used for many years as a stabilizer for polymers, it is
 subject to several drawbacks including its relatively high
 volatility, its ability to sublime and its ability to form
30 highly colored chromophores which can cause discoloration
 in polymers, polymer foams and materials in contact with

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1 the polymers. Accordingly, many investigations have been
undertaken to modify the chemistry of BHT to eliminate or
mitigate the aforementioned drawbacks or to replace BHT
entirely with some other stabilizer of equivalent or
5 superior effectiveness.

Oxidative stabilizers similar in structure and
utility to the functionalized esters derived from (4-
hydroxy-3,5-dialkylphenyl)alkanoic acids are disclosed in
U.S. Patent Nos. 3,644,482, 3,779,945 and 4,032,562. In
10 U.S. Patent No. 3,644,482, the alkanolic acid esters are
terminated with aliphatic hydrocarbons which is not the
case in the compounds of the reaction product mixtures of
the instant invention. The compounds of U.S. Patent No.
3,644,482 are isolated and crystallized which may be
15 contrasted with the liquid mixtures of the present
invention.

U.S. Patent No. 3,779,945 discloses stabilizer
compositions containing mixtures of 3-(3,5-dialkyl-4-
hydroxyphenyl)propionic acid esters of at least two non-
20 identical alkanediols.

U.S. Patent No. 4,032,562 discloses phenolic
stabilizers, indicated for use in polymers such as
polyurethanes, which are obtained by reacting a 3,5-
dialkyl-4-hydroxyphenylalkanoic acid, acid chloride or
25 lower alkyl ester with a saturated aliphatic glycol under
known esterification conditions employing as catalyst a
strong acid such as para-toluene sulfonic acid. In all of
the working examples, the reaction product (which would
necessarily have contained a complex mixture of
30 esterification products) was subjected to distillation to
yield what appears to have been a single relatively pure

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1 product or narrow fraction of closely related products.
However, being relatively pure or being made up of closely
related compounds, the distilled reaction products of U.S.
Patent No. 4,032,562 are prone to crystallizing into a
5 solid mass which is difficult to manage, especially where
addition of the product to a liquid polymer such as a
polyalkylene glycol or to a liquid reaction mixture
providing a solid polymer, e.g., a reaction mixture
providing a rigid or semirigid polyurethane slabstock, is
10 concerned. There is no suggestion in U.S. Patent No.
4,032,562 of stabilizing a liquid polymer with the entire,
i.e., the undistilled or unfractionated product, of the
foregoing esterification reaction.

15 SUMMARY OF THE INVENTION

In accordance with the present invention, a method for stabilizing an organic material that is subject to thermal and/or oxidative deterioration is provided which comprises incorporating into such material a stabilizing amount of a liquid, crystallization-resistant mixture of phenolic esters made up predominantly of phenolic monoester(s), the mixture of phenolic esters being obtained by reacting an alkyl ester of a 3,5-dialkyl-4-hydroxyphenyl alkanolic acid with a polyhydroxyl alcohol under esterification reaction conditions employing an esterification reaction catalyst.

The liquid, crystallization-resistant stabilization composition employed in the method of the present invention possesses a decided advantage over stabilizers such as the distilled esterification products disclosed in U.S. Patent No. 4,032,562 that may be

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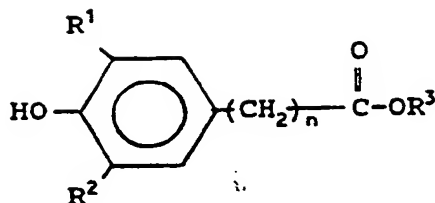
1 initially liquid but which tend to crystallize during
subsequent handling, transit or storage. Thus, the
stabilization composition herein is more apt to remain
liquid when its use is desired. In the case of a
5 stabilizer composition that has solidified due to
crystallization, heating is required to return the
composition to the liquid state before it can be added to
the organic material requiring stabilization, an
inconvenience at best and a technically troublesome
10 requirement at worst.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The stabilizer composition of this invention is
obtained by reacting at least one alkyl ester of a 3,5-
15 dialkyl-4-hydroxyphenyl alkanolic acid with at least one
polyhydroxyl alcohol under esterification reaction
conditions employing an esterification catalyst. The
resulting reaction product comprises a complex mixture of
functionalized esters of the 3,5-dialkyl-4-hydroxyphenyl
20 alkanolic acid which are not distilled, fractionated or
separated from each other to any appreciable extent prior
to being added to the organic material requiring
stabilization. Laboratory and chromatographic analyses
reveal that the mixture of esters contains hydroxy and C₂-
25 C₁₂ alkoxy functionalized 3-(3',5'-di-t-butyl-4'-
hydroxyphenyl)alkanoic acid esters of the polyhydroxyl
alcohol.

The starting alkyl esters of 3,5-dialkyl-4-
hydroxyphenyl alkanolic acid are preferably selected from
30 among those of the general formula

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wherein R¹, R² and R³ each is the same or different and represents an alkyl group of from 1 to 6 carbon atoms and n is 0, 1 or 2. Preferred starting phenolic esters include those in which R¹ and/or R² are relatively bulky groups such as t-amyl, t-butyl, etc. The compounds methyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, ethyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate and propyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate are especially preferred.

The starting polyhydroxyl alcohols are preferably selected from among the aliphatic polyhydroxyl alcohols of the general formula R(OH)_n wherein R is an aliphatic group of from 2 to about 12 carbon atoms and n is 2 to 7. Representative of the preferred group of aliphatic polyhydroxyl alcohols are such compounds as ethylene glycol, the propanediols, the butanediols, the pentanediols, the hexanediols, the heptanediols, the octanediols, glycerol, trimethylol propane, pentaerythritol, etc., and combinations of any of the foregoing. In the case of ethylene glycol, it may be advantageous to include another polyhydroxyl alcohol reactant so as to obtain a reaction product having greater crystallization resistance than that obtainable employing ethylene glycol alone. Diols possessing a secondary

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1 hydroxyl group such as 1,2-propanediol and 1,3-butanediol
and triols such as glycerol are especially preferred for
use herein. Such alcohols tend to provide mixtures of
phenolic esters having greater resistance to
5 crystallization.

While the mole ratio of polyhydroxyl alcohol to
phenolic ester reactant can be less than, equal to or
greater than 1, it is generally desirable to use a molar
excess of the alcohol as this is likely to increase the
10 amount of phenolic monoester(s) in the reaction product.
In general, the mole ratio of polyhydroxyl alcohol to
phenolic ester can vary from about 1.2:1 to about 10:1,
preferably from about 1.5:1 to about 6:1 and more
preferably from about 1.7:1 to about 4:1. Suitable
15 reaction temperatures can range from about 100° to about
190°C and preferably from about 120° to about 175°C.

Other reaction conditions that may affect the
outcome of the reaction and the nature of the product
mixture include the type of esterification catalyst used.
20 Although both basic and acidic esterification catalysts
can be used, it is generally preferred to employ an acidic
catalyst such as p-toluene sulfonic acid, especially when
the polyhydroxyl alcohol reactant contains a secondary
hydroxyl group, so as to provide reaction mixtures of the
25 greatest complexity, in turn providing mixtures of
phenolic esters having the greatest crystallization
resistance. Whatever the esterification catalyst used, it
can generally be employed at from about 0.1 to about 10,
and preferably from about 0.5 to about 2.0, mole percent
30 of the starting phenolic ester. The reaction time will
ordinarily be on the order of from about 4-5 hours.

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- 1 Monitored by gas chromatographic methods, the reaction can
be allowed to continue until the remaining phenolic ester
reactant possesses an area percent of less than about 5%,
preferably less than about 2% and more preferably less
5 than about 1%.

The mixed phenolic ester stabilizer composition
herein can be made up entirely of the product phenolic
esters but can also contain substantial quantities of one
or more other stabilizers, e.g., other phenolic
10 stabilizers, amine-containing stabilizers, thioester
stabilizers, phosphite stabilizers, etc.

Amine-containing stabilizers that can be used
herein include the complex mixture of substituted
diphenylamines containing a significant proportion of
15 butylated and oxylated species which is obtained by
reacting isobutylene and diphenylamine. These substituted
diphenylamines are commercially available under the
tradenames Naugard PS-30 (Uniroyal Chemical Co.) and
Irganox L-57 (Ciba-Geigy Corporation). Other substituted
20 diphenylamine stabilizers that can be used herein include
Wingstay 29 (Goodyear) and Vulkanox (Mobay). Still other
amine stabilizers include the phenylenediamines and
mixtures of phenolic and phenylenediamine stabilizers such
as are known in the art.

25 Examples of thioester stabilizers that can be
used herein include Cyanox 711 (American Cyanamid), Argus
DMTDP (Argus Chemical Co.) and Evanstab 14 and Carstab
DMTDP (Evans).

Other useful stabilizers than can be added to
30 the mixed phenolic ester stabilizer composition of this
invention include the thiophenols, dimethylacridan,

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1 phenothiazine and phosphites such as phenyl diisodecyl
phosphite, tris(nonylphenyl)phosphite and, more recently,
tris(2,4-di-t-butylphenyl)phosphite which has become the
industry standard for hydrolytic stability.

5 In carrying out the method of the invention, a
stabilizing amount of the stabilizing composition is added
to an organic material which is susceptible to thermal
and/or oxidative degradation. In particular, synthetic
organic polymeric substances such as vinyl resins formed
10 from the polymerization of vinyl halides or from the
copolymerization of vinyl halides with unsaturated
polymerizable compounds can be stabilized with the
mixtures of functionalized esters of this invention.
Specifically, these vinyl compounds would include vinyl
15 esters, alpha, beta-unsaturated acids, esters, aldehydes,
ketones and unsaturated hydrocarbons such as butadiene or
styrene.

The method of this invention is also applicable
to the stabilization of poly-alpha-olefins such as
20 polyethylene, polypropylene, polybutylene, polyisoprene,
and the like and copolymers of poly-alpha-olefins,
polyamides, polyesters, polycarbonates, polyacetals,
polystyrene and polyethyleneoxide. Included as well are
high-impact polystyrene copolymers such as those obtained
25 by copolymerizing butadiene and styrene and those formed
by copolymerizing acrylonitrile, butadiene and styrene.

Other organic materials stabilized in accordance
with the present invention include aliphatic ester
lubricating oils, animal and vegetable-derived oils,
30 hydrocarbon materials such as gasoline, both natural and
synthetic, diesel oil, mineral oil, fuel oil, drying oil,

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1 cutting fluids, waxes, resins and fatty acids such as
soaps.

A particularly advantageous application of the
method of this invention is the stabilization of polyether
5 polyols which are thereafter reacted with isocyanates to
produce polyurethane foams. The stabilization
compositions of this invention impart scorch (both
physical and color) protection to the polyurethane foams
which are employed in such end uses as carpet underlay,
10 bedding, furniture, automobiles (both insulation and
seats) and packaging. The occurrence of scorch is of
major concern to polyurethane foam manufacturers since
scorch negatively affects the appearance of the product,
causes physical damage and can result in fire. Therefore,
15 foam manufacturers require enhanced scorch protection
during flexible slabstock foam production. The role of
antioxidants can be critical in providing increased scorch
protection in urethane foams without diminishing the other
properties desired by the industry.

20 The stabilizer composition of this invention can
be incorporated into the organic material to be stabilized
by known and conventional methods. In particular, the
stabilizer composition of this invention can be pumped or
metered into the organic material in predetermined
25 amounts. The specific amounts of stabilizer composition
employed can vary widely depending upon the particular
organic material being stabilized. In general, the
addition of from about 0.1 to about 2, preferably from
about 0.2 to about 1 and more preferably from about 0.4 to
30 about 0.6 percent, of stabilizer composition by weight of
the organic material to be stabilized provides generally

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1 good results. In the case of a polyurethane foam, such
amounts of stabilizer composition can be added directly to
a component of the polyurethane foam-forming composition,
e.g., the polyol, or to the foam-forming composition
5 itself. The following examples are illustrative of the
invention.

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EXAMPLE 1

This example illustrates the preparation of a liquid, crystallization-resistant mixed phenolic ester stabilization composition for use in the method of the invention.

A 5-liter bottom outlet reaction kettle with a flanged glass top was equipped with an overhead stirrer, a subsurface nitrogen sparge tube, a thermocouple probe and a Graham condenser. The Graham condenser was fitted with a simple distillation head and a condenser.

The vessel was charged with methyl 3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate (1880 g), 1,3-butanediol (3,090 ml) and *p*-toluene sulfonic acid monohydrate (PTSA) (12.8 g). The mole ratio of 1,3-butanediol to phenolic ester reactant was about 5.4:1. The system was purged with nitrogen, agitated and warmed to 145°C. The system was held at 145°C for 5.5 hours. The reaction mass was allowed to cool to about 80°C and thereafter Lacolene (Ashland Chemical Co.) aliphatic petroleum naphtha (750 ml) was added. The solution was initially extracted with 0.12M sodium bicarbonate (800 ml) and then extracted three times with water (200 ml portions). Any remaining volatile matter was removed by rotary evaporation. The yield of light-colored, liquid product was 1,957 g. The product obtained was a complex mixture of phenolic esters having a moderate viscosity at room temperature.

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EXAMPLE 2

1 This example illustrates another preparation of
a liquid, crystallization-resistant mixed phenolic ester
stabilization composition for use in the method of the
5 invention.

A 5-liter bottom outlet reaction kettle with a
flanged glass top was equipped with an overhead stirrer, a
subsurface nitrogen sparge tube, a thermocouple probe and
a Graham condenser.

10 The vessel was charged with methyl 3-(3,5-di-t-
butyl-4-hydroxyphenyl)propionate (2917 g), 1,3-butanediol
(1798 g), and p-toluene sulfonic acid monohydrate (19.7
g). The mole ratio of 1,3-butanediol to methyl ester was
about 2:1. The system was purged with nitrogen, agitated,
15 and warmed to 140°C. The system was held at 140°C for 9
hours. The reaction mass was allowed to cool to about
80°C and thereafter Lasolene (Ashland Chemical Co.)
aliphatic petroleum naphtha (600 ml) was added. The
solution was extracted five times with water (800 ml
20 portions). Any remaining volatile matter was removed by
rotary evaporation. The product obtained was a light-
colored, complex mixture of phenolic esters having a
moderate viscosity at room temperature.

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COMPARATIVE EXAMPLE 1

This example illustrates the preparation of an essentially pure phenolic ester or mixture of closely related phenolic esters as described in U.S. Patent No. 4,032,562, discussed above.

A 2-liter bottom outlet reaction kettle with a flanged glass top was equipped with an overhead stirrer, a subsurface nitrogen sparge tube, a thermocouple probe, an inlet from a heated reservoir, and a Graham condenser. The Graham condenser was fitted with a simple distillation head and a condenser.

The reaction kettle was charged with 994.9 grams of 1,3-butanediol. Thereafter, 1128 grams of methyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate was charged into the reservoir and 7.15 grams of lithium amide was added to the reaction kettle. The entire system was purged with nitrogen and the methyl 3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate was heated until it melted. The temperature of the Graham condenser was adjusted to 65-70°C and the butanediol was heated to 150°C. The methyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate was added over three hours with agitation and nitrogen sparge. Heat treatment of the reaction mass was continued for an additional four hours.

The reaction mass was brought to 80°C followed by addition of 250 ml of xylenes. This was followed by the addition of glacial acetic acid (30 ml). The mixture was agitated, allowed to settle and the aqueous layer was removed. The mixture was washed with 400 ml of water, with 500 ml of 0.55 M sodium bicarbonate and twice more with 400 ml portions of water.

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1 Water, xylene and other volatiles were removed
by distillation at 60 torr at temperatures ranging from
about 50 to about 130°C. The yield was 1250 grams of a
dark liquid mixture of phenolic esters.

5 Such mixture is not suitable for use as an
antioxidant or stabilization additive since its dark color
would only discolor the material to which it is added.
For example, were the dark liquid added to a polyether
polyol which in turn were to be used in the manufacture of
10 a polyurethane foam, the resulting foam would exhibit a
decided discoloration which would be commercially
unacceptable. Therefore, the usual practice, and one
followed in U.S. Patent No. 4,032,562, is to distill the
dark liquid to obtain a relatively clear product made up
15 of a single pure phenolic ester or mixture of closely
related (in terms of boiling point) phenolic esters. In
the present example, the dark liquid mixture of phenolic
esters was purified by distillation at 3 torr to a
constant boiling point of 197°C.

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EXAMPLES 3-7

5 Polyurethane foams stabilized with known stabilization compositions and with the mixed phenolic ester stabilization compositions of the present invention were prepared for comparison, specifically, for the degree of scorch protection provided by the stabilizers.

10 The polyurethane foam-forming reaction mixtures were prepared with a 3,000 average molecular weight Olin Poly-G 32-52 polyether polyol (Olin Corp.) minimally stabilized against degradation with 100 ppm of Naugard BHT (Uniroyal Chemical Company, Inc.) and further stabilized with 2000 ppm of Naugard PS-30 amine stabilizer (Uniroyal Chemical Company, Inc.). To 200g of Olin Poly-G 32-52 polyether polyol was added with stirring a premix
15 containing 10g water, 0.20g Dabco-33LV amine catalyst (Air Products Co.), 2.9g L-620 silicone surfactant (Union Carbide, Inc.) and 14g Antiblaze 100 flame retardant (Albright & Wilson Americas). To this mixture were added 0.0146g of T-10 tin catalyst (Air Products and Chemicals)
20 with stirring for 5 additional seconds. Finally, 131.2g of TDI-80, a 115 index toluene diisocyanate (Mobay Corp.) was added.

25 The reaction mixture was stirred at high speed for 7 additional seconds and then poured into a 10" x 10" x 5" cardboard box.

The foam was allowed to rise completely at room temperature, indicated by the appearance of bubbles across the surface of the foam bun, and then allowed to stand for 5 additional minutes. The sides of the box were removed
30 before curing the sample for 17.5 minutes at 20% power in a GE Whirlpool microwave oven. The foams were air oven

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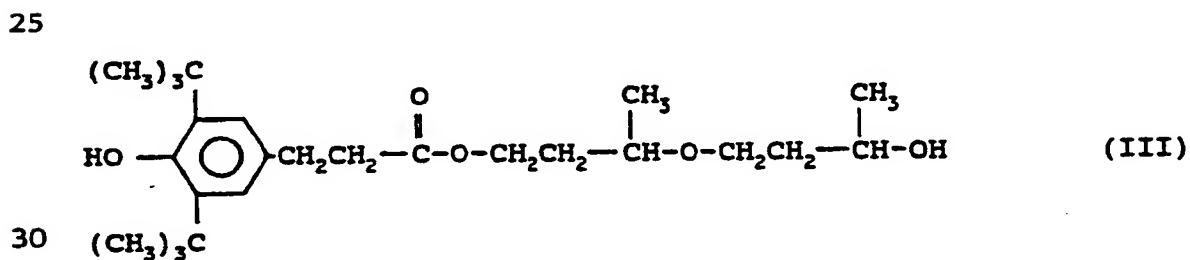
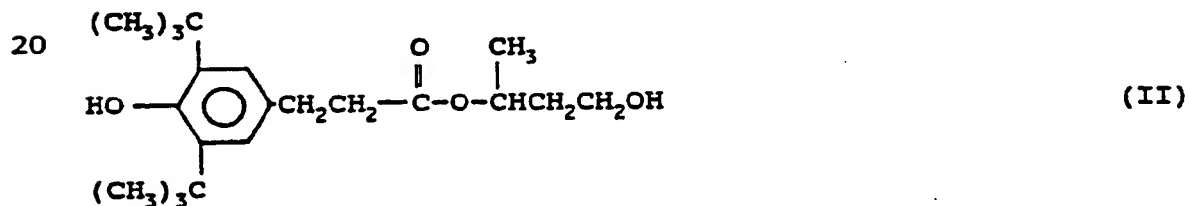
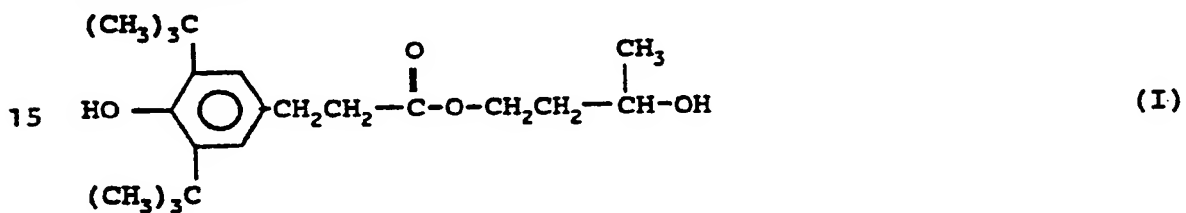
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1 cured for 3 minutes at 125°C immediately after the
microwave cure.

Upon removal of a foam from the air circulating
oven, the foam was immediately cut in half, horizontally
5 to the rise of the foam, and analyzed for degree of scorch
using the Hunterlab Colorimeter, Model D25M/L.

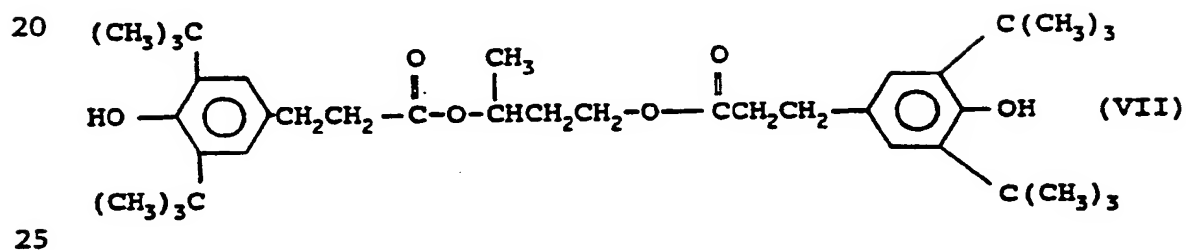
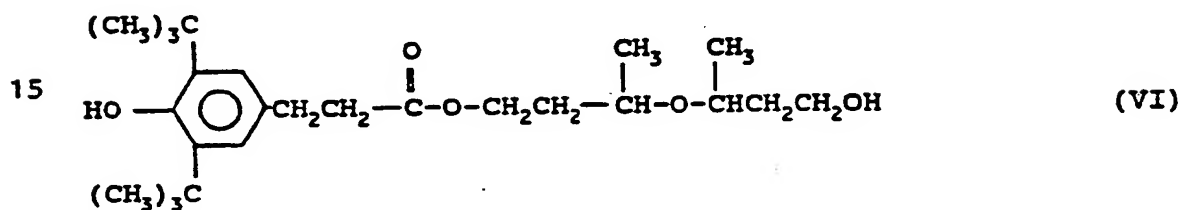
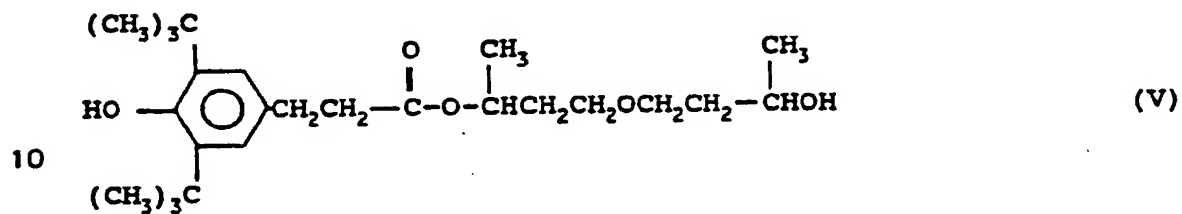
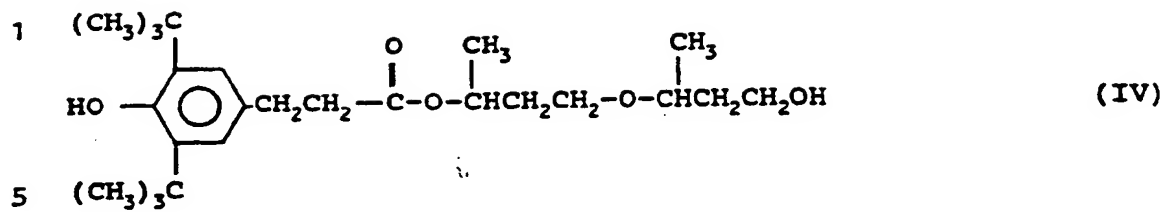
The performance rating of each foam is based on
a scale of 1-10 with 1 being the best scorch protection
and 10 being the worst.

10 The phenolic ester stabilizer compositions used
in the foams contained various mixtures of the following
compounds:



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The compositional analysis and amount of each stabilizer composition employed in each polyurethane foam-forming reaction mixture and resulting foam were as follows:

Example	Analysis of Stabilizer		Amount of Added Stabilized Composition, ppm
	Compound(s)	Area %*	
3 (standard)	BHT		2500
4 (essentially I + II identical to the distillate from Comp. Ex. 1)		98.6	2500
5	I + II	68	2500
	III to VI	23	
	VIII	4	
15	Other compound(s)	5	
6	I + II	80	2500
	III to VI	13	
	Other compound(s)	7	
7	I + II	50	2500
	III to VI	29	
	VII	11	
20	Other compound(s)	10	

*Area % by GC analysis.

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1 The results of the scorch test for each of
two separate runs were as follows:

<u>Scorch Rating</u>			
	<u>Example</u>	<u>Run No. 1</u>	<u>Run No. 2</u>
5	3	2+	2+
	4	4	3
	5	2	1-2
	6	2+	2+
	7	Not Run	1-2

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 These data show that the mixed phenolic ester
stabilization composition of this invention performed at
least as well, and in some cases better, than the industry
standard, BHT, and that the composition consistently out-
15 performed a relatively pure phenolic ester or mixture of
closely related phenolic esters (Example 3) which is
illustrative of the prior art.

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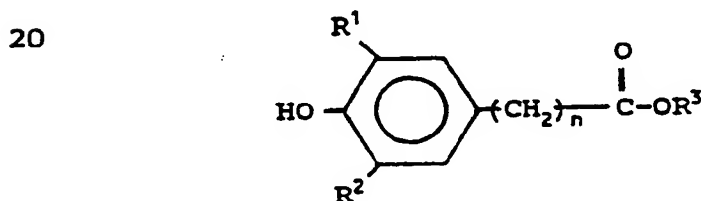
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1 WHAT IS CLAIMED IS:

1. A method for stabilizing an organic material which is subject to thermal and/or oxidative deterioration which comprises incorporating into such material a stabilizing amount of a liquid, crystallization-resistant mixture of phenolic esters made up predominantly of phenolic monoester(s), the mixture of phenolic esters being obtained by reacting an alkyl ester of a 3,5-dialkyl-4-hydroxyphenyl alkanolic acid with a polyhydroxyl alcohol under esterification reaction conditions employing an esterification reaction catalyst.

2. The method of Claim 1 wherein the organic material which is subject to deterioration is selected from the group consisting of polyether polyol and polyurethane.

3. The method of Claim 1 wherein the alkyl ester of the 3,5-dialkyl-4-hydroxyphenyl alkanolic acid possesses the general formula



25 wherein R¹, R² and R³ each is the same or different and represents an alkyl group of from 1 to 6 carbon atoms and n is 0, 1 or 2 and the polyhydroxyl alcohol possesses the general formula R(OH)ₙ wherein R is an aliphatic group of
30 from 2 to about 12 carbon atoms and n is from 2 to about 7.

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1 4. The method of Claim 3 wherein the
polyhydroxyl alcohol is a diol possessing a secondary
hydroxyl group or a triol.

5 5. The method of Claim 3 wherein the
esterification catalyst is an acidic esterification
catalyst.

6. The method of Claim 3 wherein the mole
ratio of polyhydroxyl alcohol to the alkyl ester of the
3,5-dialkyl-4-hydroxyphenyl alkanoic acid is from about
10 1.2:1 to about 10:1.

7. The method of Claim 3 wherein the mole
ratio of polyhydroxyl alcohol to the alkyl ester of the
3,5-dialkyl-4-hydroxyphenyl alkanoic acid is from about
1.5:1 to about 6:1.

15 8. The method of Claim 3 wherein the
polyhydroxyl alcohol is a diol possessing a secondary
hydroxyl group or a triol, the esterification catalyst is
an acidic esterification catalyst and the mole ratio of
polyhydroxy alcohol to the alkyl ester of the 3,5-dialkyl-
20 4-hydroxyphenyl alkanoic acid is from about 1.2:1 to about
10:1.

9. The method of Claim 8 wherein the aliphatic
polyhydroxyl alcohol is 1,2-propanediol, 1,3-butanediol or
glycerol and the alkyl ester of the 3,5-dialkyl-4-
25 hydroxyphenyl alkanoic acid is methyl 3-(3,5-di-t-butyl-4-
hydroxyphenyl)propionate, ethyl 3-(3,5-di-t-butyl-4-
hydroxyphenyl)propionate or propyl 3-(3,5-di-t-butyl-4-
hydroxyphenyl)propionate.

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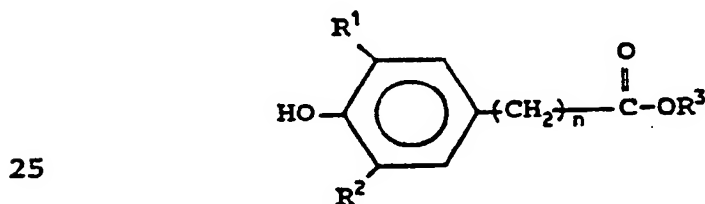
-22-

1 10. The method of Claim 8 wherein the organic
material which is subject to deterioration is selected
from the group consisting of polyether polyol and
polyurethane.

5 11. A composition comprising an organic
material which is subject to thermal and/or oxidative
deterioration and a stabilizing amount of a liquid,
crystallization-resistant mixture of phenolic esters made
up predominantly of phenolic monoester(s), the mixture of
10 phenolic esters being obtained by reacting an alkyl ester
of a 3,5-dialkyl-4-hydroxyphenyl alkanolic acid with a
polyhydroxyl alcohol under esterification reaction
conditions employing an esterification reaction catalyst.

15 12. The method of Claim 11 wherein the organic
material which is subject to deterioration is selected
from the group consisting of polyether polyol and
polyurethane.

20 13. The method of Claim 11 wherein the alkyl
ester of 3,5-dialkyl-4-hydroxyphenyl alkanolic acid
possesses the general formula



wherein R^1 , R^2 and R^3 each is the same or different and
represents an alkyl group of from 1 to 6 carbon atoms and
30 n is 0, 1 or 2 and the polyhydroxyl alcohol possesses the

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1 general formula $R(OH)_n$ wherein R is an aliphatic group of
from 2 to about 12 carbon atoms and n is from 2 to about
7.

14. The method of Claim 13 wherein the
5 polyhydroxyl alcohol is a diol possessing a secondary
hydroxyl group or a triol.

15. The method of Claim 13 wherein the
esterification catalyst is an acidic esterification
catalyst.

10 16. The method of Claim 13 wherein the mole
ratio of polyhydroxyl alcohol to the alkylation of the
3,5-dialkyl-4-hydroxyphenyl alkanoic acid is from about
1.2:1 to about 10:1.

17. The method of Claim 13 wherein the mole
15 ratio of polyhydroxyl alcohol to the alkyl ester of the
3,5-dialkyl-4-hydroxyphenyl alkanoic acid is from about
1.5:1 to about 6:1.

18. The method of Claim 13 wherein the
aliphatic polyhydroxyl alcohol is a diol possessing a
20 secondary hydroxyl group or a triol, the esterification
catalyst is an acidic esterification catalyst and the mole
ratio of polyhydroxy alcohol to the alkyl ester of the
3,5-dialkyl-4-hydroxyphenyl alkanoic acid is from about
1.2:1 to about 10:1.

25 19. The method of Claim 18 wherein the
aliphatic polyhydroxyl alcohol is 1,2-propanediol, 1,3-
butanediol or glycerol and the alkyl ester of the 3,5-
dialkyl-4-hydroxyphenyl alkanoic acid is methyl 3-(3,5-di-
t-butyl-4-hydroxyphenyl)propionate, ethyl 3-(3,5-di-t-
30 butyl-4-hydroxyphenyl)propionate or propyl 3-(3,5-di-t-
butyl-4-hydroxyphenyl)propionate.

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1 20. The method of Claim 18 wherein the organic
material which is subject to deterioration is selected
from the group consisting of polyether polyol and
polyurethane.

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INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/US 94/03037A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08K5/13

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 032 562 (MARTIN DEXTER) 28 June 1977 cited in the application see column 1, line 13 - line 40 see examples 1-3 ---	1-20
A	EP,A,0 141 419 (B.F. GOODRICH COMPANY) 15 May 1985 see page 30, line 31 - line 32 see page 31, line 19 - line 20 see claim 1 -----	1-20

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

19 July 1994

Date of mailing of the international search report

- 8. 08. 94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

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Siemens, T

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. Application No

PCT/US 94/03037

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		CA-A- 1325217	14-12-93
		DE-A- 3469732	14-04-88
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		JP-A- 60112737	19-06-85